

# **Lixiviant Tests to Assess Leachability of Cesium-137 from West Jefferson North Site Soils**

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**April, 2003**

**Prepared for the U.S. Department of Energy  
Under Contract DE-AC06-76RLO 1830**

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## Executive Summary

Radionuclide ( $^{137}\text{Cs}$ ) contaminated glacial till soils from the JN site of the Battelle's Nuclear Sciences Area at West Jefferson, Ohio, are slated to be remediated by using soil flushing technology (Well Injection Depth Extraction – WIDE<sup>TM</sup>). For soil flushing to be successful at this site an effective lixiviant is needed to mobilize  $^{137}\text{Cs}$  from these fine textured soils. We conducted a set of tests on three soil samples (Batch I, II, and III) to assess the effectiveness of a Cesium-specific lixiviant (developed at Pacific Northwest National Laboratory) for mobilizing  $^{137}\text{Cs}$  from the soils at the JN site. We also determined selective physical, chemical, mineralogical and radiochemical properties of these soils.

The results indicated that the Batch II and III soil materials were fine-textured with silt and clay content of ~70%, whereas, Batch I soil was well-graded with silt and clay content of 45%. The organic carbon contents of all three soil samples were similar (~1 - 2%), except that Batch I soil contained 2 – 3 times more inorganic carbon than Batch II soil. The dominant minerals in these soils were quartz and dolomite, calcite, and hornblende with minor quantities of feldspar, mica, chlorite and smectite. Batch I material contained more dolomite and calcite, whereas, the Batch II soil contained relatively higher proportions of mica and hornblende than the Batch I soil.

Activity of  $^{137}\text{Cs}$  was measured to be 609, 26.5, and 10.5 pCi/g in Batch I (3-bag composite), Batch II, and Batch III soils respectively. A major fraction of  $^{137}\text{Cs}$  activity (~88% of the total activity) in Batch II, and III soils were present in silt and clay fractions (~70% of mass). The sand and gravel fractions constituting ~30% of Batch II, and III soil masses contained only ~13% of the total  $^{137}\text{Cs}$  activity in these soils. Selective extractions with specific electrolytes were relatively ineffective in mobilizing  $^{137}\text{Cs}$  indicating that almost all of this contaminant in these soils is in recalcitrant (immobilized) forms such as, in interlayer edge and structural sites of micas.

Three successive extractions conducted at 90 °C using the PNNL lixiviant removed a total of ~66% of initial activity from Batch I soil resulting in a residual  $^{137}\text{Cs}$  activity of about 210 pCi/g. in soil. The data indicated that the PNNL lixiviant was effective in mobilizing and removing significant fractions of relatively recalcitrant forms of  $^{137}\text{Cs}$  in this soil. A single extraction using an enhanced PNNL lixiviant composition removed about 43 – 57% of the  $^{137}\text{Cs}$  activity from Batch II soil with resulting residual soil activities of 11.5 - 15.2 pCi/g.

Lixiviant optimization batch experiments conducted at 90 °C using Batch I soil (containing the highest  $^{137}\text{Cs}$  activity at the JN site) indicated that a maximum fraction (~40%) of  $^{137}\text{Cs}$  can be mobilized with the minimum concentrations of lixiviant components consisting of ~0.25M HH, ~1M CA, and 0.3M of NC respectively.

Dynamic flow tests conducted using the optimized PNNL lixiviant indicated that the maximum fraction of  $^{137}\text{Cs}$  extractable from Batch I soil under flow-through conditions was ~28% as compared to a maximum of ~40% extraction achieved in batch extraction experiments. These data indicated that to achieve maximum  $^{137}\text{Cs}$  mobilization of ~28% from Batch I type soil, (containing high  $^{137}\text{Cs}$  activity), it would be necessary to advectively-flow at least ~20 bed volumes of optimized lixiviant at 90 °C through the soil column.



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# **LIXIVANT TESTS TO ASSESS LEACHABILITY OF CESIUM-137 FROM WEST JEFFERSON NORTH SITE SOILS, OHIO**

## **INTRODUCTION**

Soil flushing is a remediation technology aimed at removing inorganic, organic, and radionuclide contaminants to the extent that the residual levels of these contaminants in the treated soil are below selected safe levels. The effectiveness of soil flushing as a remediation technique depends mainly on the type of binding processes that exists between the contaminants and the soil particles. Contaminants in soils may be found adsorbed or precipitated on the soil mineral surfaces or as distinct particles. If a contaminant exists mainly in the adsorbed form, the finer soil particle fractions tend to contain higher concentrations of that contaminant. This phenomenon can be attributed to the fact that finer soil particles possess greater surface areas per unit mass than the coarser sized fractions.

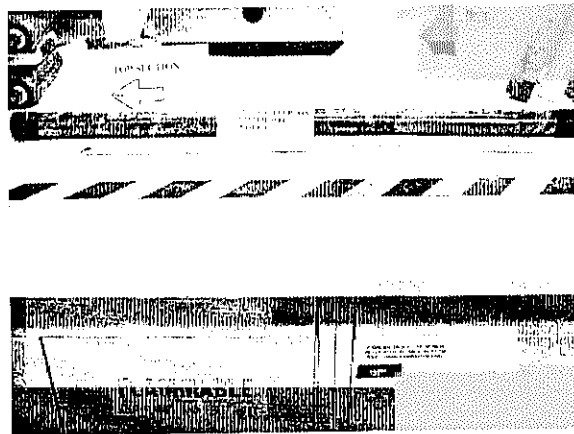
The objective of this study was to characterize samples of radionuclide contaminated glacial till soils from the JN site of the Battelle's Nuclear Sciences Area at West Jefferson, Ohio, and to test the effectiveness of a PNNL lixiviant for removing  $^{137}\text{Cs}$  from this soil. The results of these tests will be used to assess whether the lixiviant can be used as part of soil flushing technology (Well Injection Depth Extraction – WIDE<sup>TM</sup>, Quaranta, 2001) that will be deployed to remediate the soils at this site.

## **MATERIALS AND METHODS**

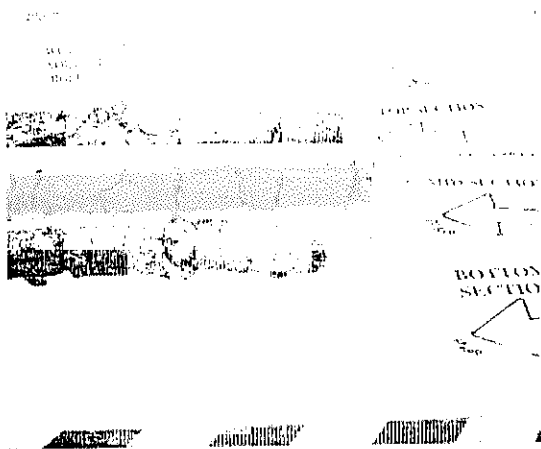
### **Soil Samples**

Soil samples from the JN site from West Jefferson, Ohio were received in three separate batches. Detailed geology, hydrogeology and the description of the soils at the JN site can be obtained from a previously published report (Beard and Gupta, 1990). Batch I material (designated as BRM-7824) was received during 4/2001 and Batch II soil sample (designated as BRM-7886) was received during 6/2001. Later (2/2002), Batch III soil samples (designated as BRM-8152) were shipped and received at PNNL. Gamma spectrometry data transmitted with the samples indicated that BRM-7824 material had about twenty times higher  $^{137}\text{Cs}$  activity (~855 pCi/g) as compared to the BRM-7886 soil sample (~39.9 pCi/g).

Soil samples labeled Batch I and Batch II were received in sealed 5- gallon containers. Each of these samples was packed in three separate bags. Batch III soil samples were received in about four foot long sealed plastic tubes (Figure 1). Batch I and Batch II material were prepared for analyses by compositing equal masses of material from each container. The samples Batch III soil were prepared for analyses by extruding the soil cores from the tubes (Figure 2), removing vegetative matter such as, surface herbaceous layers and roots and very coarse gravelly materials. Next, Batch III soil was homogenized and stored in sealed containers to preserve the natural moisture content.



**Figure 1.** Sealed Batch III Soil Sample Cores from JN Site



**Figure 2.** Extruded Batch III Soil Samples from JN Site that reveal various Soil Horizons

One of the soil horizons from Batch II material contained tan colored nodules, which were isolated and analyzed separately for their carbon content and mineralogy. Subsamples of each batch of soil were drawn as required for various tests.

### **Gravimetric Moisture content**

The gravimetric field moisture content of the soil samples were determined using a standard procedure (Gardner, 1986). Three ~20-g portions of soil subsamples were transferred to tared containers, oven-dried at  $105 \pm 5$  °C for 24 hours, cooled over a desiccant, and weighed. The gravimetric water content was computed as a percentage change in soil weight before and after oven-drying.

## Carbon Content

Total and inorganic carbon content of soil samples were determined using standard coulometric techniques (PNN AGG-SST-VZC Procedures 2000). Additionally, a portion of the difficult-to-disperse tan-colored nodules from Batch II soil were analyzed separately for their carbon content.

## Particle Size Distribution Analysis

Particle size distribution was determined using composited subsamples of Batch II (BRM-7824) and Batch III soils. Weighed portion of the soil was wet sieved using DI water through a sequence of sieves (#5 [4 mm], 10 [2 mm], 18 [1 mm], 35 [0.5 mm], 60 [0.25 mm], 120 [0.125 mm], and 230 mesh [0.0625 mm]). The soil fractions retained on the sieves were dried in an oven at  $105 \pm 5$  °C for 24 hours, cooled, and weighed. The silt and clay content of composited Batch I (BRM-7886) soil sample was determined by wet-sieving preweighed portions of soil using 120 and 200 mesh sieves and weighing oven-dried fractions retained on each sieve and the pan. The particle size definitions recommended by the American Society of Testing Materials (ASTM) were used in designating various size fractions (Table 1).

**Table 1.** Particle-Size Designation

Sieve Number	Particle Size (mm)	Designation
+12"	+300	Boulders
-12"/+3"	-300/+75	Cobbles
-3"/+3/4"	-75/+19	Coarse Gravel
-3/4"/+4	-19/+4.75	Fine Gravel
-4/+10	-4.75/+2.00	Coarse Sand
-10/+40	-2.00/+0.425	Medium sand
-40/+200	-0.425/+0.075	Fine Sand
-200	-0.075	Silt and Clay

Source: ASTM D2487-98.

## Mineralogical Analysis

Mineralogical analyses of soils were conducted by X-Ray Diffraction Analysis (PNNL AGG-SST-VZC Procedures 2000). Subsamples of soil (Batch I, Batch II and the tan nodules picked out of Batch II) were random-packed into aluminum sample holders and analyzed with Cu-K $\alpha$  radiation. The XRD apparatus was a Philips X'Pert MPD system (Model PW3040/00) with a Cu X-ray source operated at 45 kV, 45 mA (1.8 kW). The scan range was 2°- 40° (2 $\theta$ ) and the typical scan rate was ~2°/min. The mineralogical identification from the resulting diffraction data was made by using the program *JADE* (V5.0, V6.0, and V6.1, Materials Data Inc., Livermore, CA) and reference data from the Powder Diffraction File Database (PDF-2, International Centre for Diffraction Data, Newtown Square, PA).

## Gamma Spectrometry

Activity of  $^{137}\text{Cs}$  in bulk soil samples, selected size fractions, extracted soils, lixiviant extracts were measured using a gamma energy analysis system equipped with high-performance germanium detectors and Genie2000<sup>TM</sup> support software (PNNL AGG-SST-VZC Procedures 2000).

## Selective Extractions

The Batch I and II soil samples were treated with different electrolytes to assess the extractability of  $^{137}\text{Cs}$  associated with various mineral fractions. The extractants consisted of water, magnesium chloride, acidified hydrogen peroxide, sodium acetate and hydroxylamine hydrochloride solutions. Use of these electrolytes have been suggested (as part of a sequential extraction method) to selectively remove metal contaminants from sediments (Belzile et al., 1989). The extractions were conducted separately and the extent of  $^{137}\text{Cs}$  mobilized was determined by gamma spectrometry of the spent extractants. The types of extractants used in this procedure are listed in Table 2.

**Table 2.** Selective Extraction Scheme for JN Site Soils

Extractant	Temp (°C)	Time (min)	Type of Contaminant Association
Water	95	180	Water soluble
1N $\text{Mg}(\text{Cl})_2$ at pH 7	Ambient	30	Mg-chloride extractable
30% $\text{H}_2\text{O}_2$ , pH 2 $\text{HNO}_3$	85	300	Oxidizing acid soluble
1M $\text{CH}_3\text{COONa}$ , pH 5 $\text{CH}_3\text{COOH}$	Ambient	300	Acidic Na-Ac Soluble
0.04M $\text{NH}_2\text{OH}\cdot\text{HCl}$ +25% $\text{CH}_3\text{COOH}$	95	360	Reducible acid soluble

## Preliminary PNNL Lixiviant Tests for $^{137}\text{Cs}$ Removal

Although the PNNL lixiviant was developed to specifically remove  $^{137}\text{Cs}$  from the Hanford soils, we discovered that that the lixiviant also effectively removed other radionuclides such as  $^{60}\text{Co}$  and  $^{152}\text{Eu}$  from these soils (Mattigod et al 1994a, b). These previous studies using Hanford soils also showed that maximum  $^{137}\text{Cs}$  extraction was achieved when the extraction temperature was between 90 – 95 °C. Therefore, all the  $^{137}\text{Cs}$  removal tests on West Jefferson North Site (WJNS) soils were conducted with lixiviant temperatures set between 90 – 95 °C.

The preliminary extraction tests were conducted using both Batch I and II soil samples from JN site. The objective of this test was to assess the degree of effectiveness of PNNL lixiviant for removing  $^{137}\text{Cs}$  from relatively fine-textured JN site soils. An initial lixiviant test was conducted on Batch I sample. This test consisted of reacting the soil with PNNL lixiviant (~1:5 solid – lixiviant ratio) at 95 °C with constant agitation for 3 hours. Three successive extractions were conducted and after each extraction, the amount of  $^{137}\text{Cs}$  extracted was determined by gamma counting the liquid phase. Based on these data, additional tests were conducted on Batch II soil to determine the most effective lixiviant composition that would

optimally extract  $^{137}\text{Cs}$ . In these tests, an enhanced lixiviant was used to extract the soil and after rinsing the residual lixiviant, the soil was oven-dried and the remaining  $^{137}\text{Cs}$  activity in the soil was measured by gamma spectrometry.

### Optimization of Lixiviant Composition

The PNNL lixiviant consists of three dissolved components (HH, CA, and NC) that promote the release of  $^{137}\text{Cs}$  from soil minerals and prevent readsorption of mobilized  $^{137}\text{Cs}$ . Our previous lixiviant tests on  $^{137}\text{Cs}$ -containing soils from Hanford indicated that the maximum extraction occurred when the soils were treated for 3 h at temperatures between 90 – 95 °C. Therefore, the reaction temperature and time were held constant at (90 °C for 3 h) during the lixiviant composition optimization tests. All the tests were conducted using Batch I soil sample (containing the highest  $^{137}\text{Cs}$  activity) from the JN site. The following test matrix was used for these experiments (Table 3)

**Table 3.** Test Matrix for Lixiviant Optimization

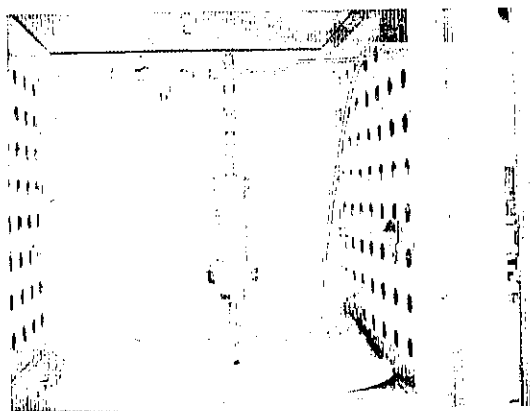
Component	Molar Concentration			
Variable HH				
	Test 1	Test 2	Test 3	Test 4
HH	0.10	0.25	0.50	0.75
CA	2.00	2.00	2.00	2.00
Variable CA				
	Test 5	Test 6	Test 7	--
HH	0.25	0.25	0.25	--
CA	0.00	0.25	1.00	--

Note: Concentrations of NC were fixed at 0.3M.  
All tests were conducted at 90 °C for 3 h.

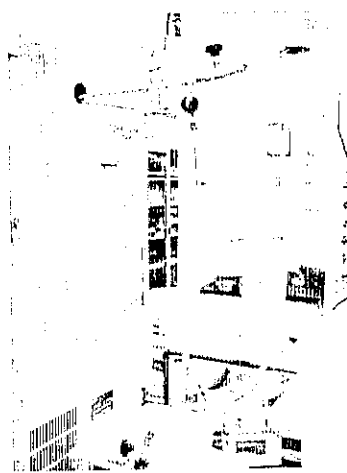
In the first set of tests, concentrations of HH was varied from 0.1 to 0.75M, and in the second set the concentrations of CA were varied from 0 – 2 M. The concentrations of NC in all tests were held constant. Some of the tests were replicated to determine the range of extraction efficiency. Typically, ~100 g (oven dry basis) of soil sample (at its natural moisture content) was reacted with ~500 ml specific lixiviant composition (~1:5 solid – lixiviant ratio) at 90 °C with constant agitation for 3 h. After extraction, the spent lixiviant was carefully removed by decantation and the soil was rinsed free of any residual lixiviant, oven-dried and the residual  $^{137}\text{Cs}$  activity in the soil was measured by gamma spectrometry.

## Lixiviant Flow-Through Tests

The dynamic flow tests were conducted using a 12 cm long stainless steel column with an internal diameter of 3.4 cm (Figure 3, 4). The bottom of the column was lined with polypropylene geotextile filter material provide by BCO (DOE 2000). These tests were conducted by packing ~30 g of Batch I soil sample into the column to a depth of 2 cm. Next, the column was filled with ~80 ml (~4.5 bed volumes) optimized PNNL lixiviant. The column was sealed both at the top and bottom and placed in an oven at 90 °C. Once the column and its contents had reached the reaction temperature, the valve at the bottom of the column was opened to initiate the flow of lixiviant through the soil mass by the pressure developed the reaction. The pressure within the column was controlled at ~20 psi during the reactive flow of the lixiviant. Additional aliquots of fresh lixiviant was flowed through the soil volume as needed to achieve total bed volumes of 9, 13.5, and 22.5 respectively. After each test, the  $^{137}\text{Cs}$  activity in spent lixiviant was determined by gamma spectrometry. In one test (9 bed volumes), the fraction of the  $^{137}\text{Cs}$  activity in the spent lixiviant present in the soil pore spaces was determined by rinsing the reacted soil with ~13.5 bed volumes of DI water and counting the wash water.



**Figure 3.** Lixiviant Extraction Column used for Batch I Soil Flow-through Tests



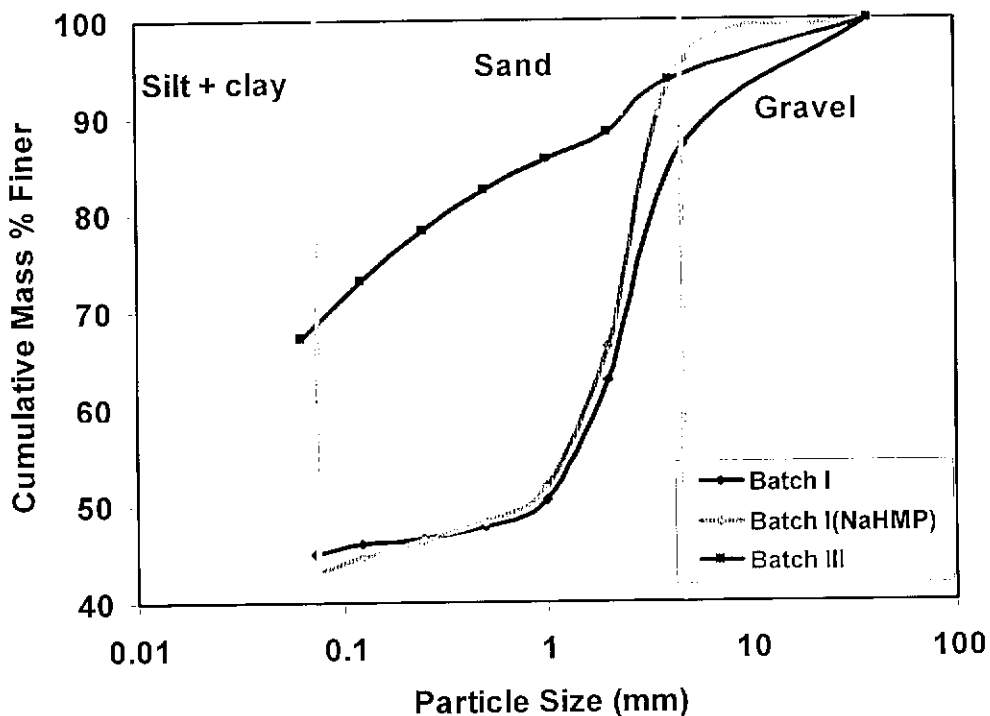
**Figure 4.** Lixiviant Injection and Collection System used for Flow-through Tests

## RESULTS AND DISCUSSION

### Physical, Chemical and Mineralogical Properties

The physical, chemical and mineralogical properties are listed in Table 4, and shown graphically in Figures 5- 7. The moisture contents of Batch I, Batch II, and Batch III soil samples were 16.8%, 22.2%, and 21.4% respectively. Texturally, Batch II and Batch III soils were finer (clay and silt content of 67 - 70%) than Batch I soil (45% clay and silt). The Batch I material appeared to be well-graded (Figure 5) in that all particle sizes appeared to be present in relatively similar proportions whereas, the predominant mass of Batch II and Batch III materials consisted of finer (silt and clay size) material. Use of sodium hexametaphosphate as a dispersant for Batch I soil promoted disaggregation and resulted in a slight decrease in gravel size particles with concomitant increase in sand size material (Figure 5). The higher moisture content of Batch II and III soils can also be attributable to the relatively finer texture of these soils relative to Batch I material.

There were no significant differences in organic carbon content of these samples (Table 4) which ranged from 0.93 – 1.76%. Relatively low organic carbon content of these soils indicated that the proportion of  $^{137}\text{Cs}$  associated with the organic fraction would be low relative to its activity associated with the inorganic mineral fraction. Data indicated that



**Figure 5.** Particle Size Distribution of Batch I and Batch III Soil Samples from JN Site



Batch I sample (6.68% inorganic carbon) contained about 3- 5 times more inorganic carbon than the Batch III (1.76%) and Batch II material (1.26%).

The dominant minerals in these soils were identified to be quartz and dolomite, calcite, and hornblende with minor quantities of feldspar, mica, chlorite and smectite (Table 4, Figure 6). The higher inorganic carbon content in Batch I material is reflected by its relatively higher contents of dolomite and calcite. The Batch II sample also contained relatively higher proportions of mica and hornblende than the Batch I and tan nodule materials. The tan nodules from Batch I soil differed from the bulk Batch I material in that these nodules contained significantly more calcite and hornblende and less mica.

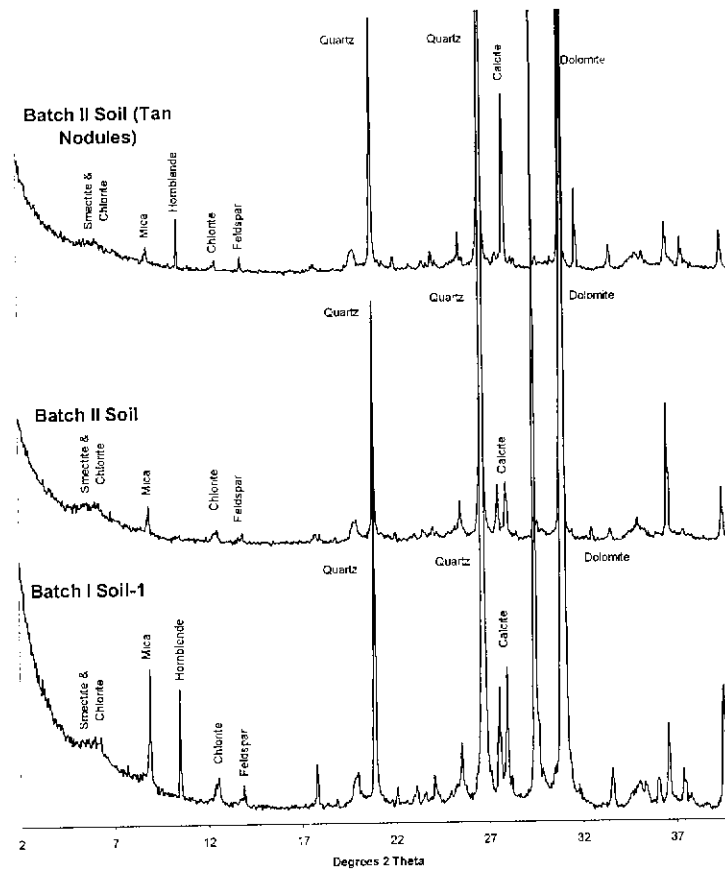
Based on a review of literature, Mattigod et al (1994 a, b) have discussed the relevancy of mineralogical properties of soils and sediments in relation to  $^{137}\text{Cs}$  fractionation and extractability. These studies listed the types minerals found in soils and the mineral sites  $^{137}\text{Cs}$  can potentially occupy (Table 5). Additionally, these authors indicated that the degree of extractability of  $^{137}\text{Cs}$  from mineral sites are in the order, exchangeable>interlayer edge>structural. According to mineralogical analyses, Batch I and Batch II soils contain mica, chlorite, smectite and feldspar. These data suggested that  $^{137}\text{Cs}$  in West Jefferson soils from the JN site may be distributed among different (exchangeable, interlayer edge and structural) types of sites therefore, would exhibit varying degrees of extractability.

**Table 4.** Physical, Chemical, and Mineralogical Properties

Soil sample	Moisture Content (%)	Particle Size distribution (wt %)		Carbon Content (%)		Mineralogy
		Clay + Silt	Sand + Gravel	Org.	Inorg.	
Batch I	16.8	45	55	0.93	6.68	Quartz, dolomite, calcite, hornblende, mica, chlorite, feldspar, smectite
Batch II	22.2	70	30	1.26	2.17	Quartz, dolomite, calcite, mica, chlorite, feldspar, smectite
Batch II (Tan nodules)	--	--	--	0.67	2.86	Quartz, dolomite, calcite, hornblende, mica, feldspar, chlorite, smectite
Batch III	21.4	67	33	1.76	2.08	--

**Table 5.** Types of  $^{137}\text{Cs}$ - Mineral Associations

Types of Sites occupied by $^{137}\text{Cs}$	Minerals
Exchangeable	Smectite, chlorite, kaolinite, Fe-oxide, humates
Interlayer edge	micas, vermiculite
Structural	feldpars, micas

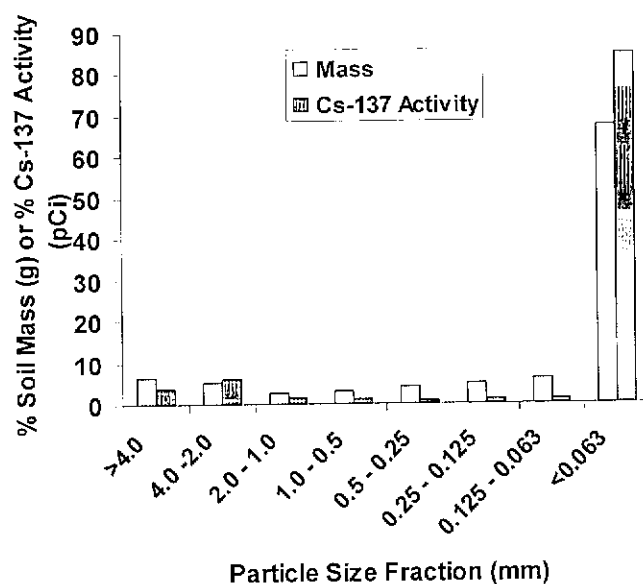


**Figure 6.** X-ray Diffraction Data for JN Site Soils

### Activity of $^{137}\text{Cs}$ in Bulk and Particle Size Fractions

The gamma spectrometry data indicated that the Batch I soil material (Table 6), which is typical of “hot spot” soils at the West Jefferson site, contained  $^{137}\text{Cs}$  activity of 609 pCi/g (3-bag composite) as compared to the 26.5 pCi/g in Batch II material (which is typical of the bulk of soil material at this site) and Batch III material (10.5 pCi/g). The activity distribution measurements (Table 6, Figure 7) indicated that, major fractions of  $^{137}\text{Cs}$  activities (~85 - 88% of the total activity) in Batch II and III soils reside in silt and clay fractions (~67 - 70% of mass). The sand and gravel fractions of these soils (Batch II and III) which constituted ~30 - 33% of soil masses contained only ~13 - 15 % of the total  $^{137}\text{Cs}$  activities in these soils.

These data suggested that for instance, even if all the  $^{137}\text{Cs}$  activities associated with sand and gravel fractions in Batch II and III soil are removed, the bulk activities in Batch II and Batch III soils would be reduced from 26.6 to 23.1 pCi/g and 10.5 to 8.9 pCi/g respectively. Therefore, any significant reduction (for instance, ~50%) in total  $^{137}\text{Cs}$  activity in these soils can be attained only if at least ~42 % the activity associated with the silt and clay size fraction is removed.



**Figure 7.** Mass and  $^{137}\text{Cs}$  Activity distribution in various Size-Fractions of Batch III Soil Sample from JN Site.

**Table 6.** Activity of  $^{137}\text{Cs}$  in Bulk and Size-fractionated Soil Samples

Sample	Bulk <sup>a</sup> (pCi/g)	Silt+clay (pCi/g)	Sand+gravel (pCi/g)	Percent of total Act (silt+clay)	Percent of total Act (sand+gravel)
Batch I	609.0 <sup>b</sup>	--	--	--	--
Batch II	26.5 <sup>c</sup>	40.2	13.6	87.3	12.7
Batch III	10.5 <sup>d</sup>	19.3	7.2	84.6	15.4

<sup>a</sup>Bulk activity numbers submitted with the soil samples from BCO were 855 pCi/g for Batch I and 39.9 pCi/g for Batch II respectively.

<sup>b</sup>Activity of sample composited from all three bags.

<sup>c</sup>Bulk activity calculated from size fraction data was 32.2 pCi/g

<sup>d</sup>Bulk activity calculated from size fraction data was 15.3 pCi/g

### Selective Extractions

The results of selective extractions indicated that these electrolytes were relatively ineffective in mobilizing  $^{137}\text{Cs}$  from the West Jefferson Site soils (Table 7). Contrastingly, previous extractions of very coarse-textured Hanford Site soils had mobilized about 8 – 21% of  $^{137}\text{Cs}$  with oxidizing acid treatment and about 3 – 16% with reducible acid extraction (Mattigod 1994).

a, b). The negligible extractability of  $^{137}\text{Cs}$  in the West Jefferson Site soils indicated that this contaminant is in recalcitrant (immobilized) forms such as in interlayer edge and structural sites of micas. These data also indicated that it would be necessary to use specifically-designed lixiviants to mobilize and remove the recalcitrant forms of  $^{137}\text{Cs}$  from these soils.

### Preliminary Lixiviant Tests for $^{137}\text{Cs}$ Removal

Data from the PNNL lixiviant tests on Batch I soil material indicated that each of the three successive extractions removed about 22% of initial  $^{137}\text{Cs}$  activity (Table 8). Cumulatively, all the three extractions removed a total of ~66% of initial activity from the soil resulting in a residual  $^{137}\text{Cs}$  activity of ~210 pCi/g. These results indicated that the lixiviant was very effective in mobilizing and removing significant fractions of relatively recalcitrant forms of  $^{137}\text{Cs}$  in this soil.

Based on these results, the PNNL lixiviant composition was modified to extract significantly more  $^{137}\text{Cs}$  activity in a single extraction step. These tests conducted on lower activity Batch II soil material indicated that with modified lixiviant, about 43 – 57% of the  $^{137}\text{Cs}$  activity can be removed from the soil resulting in residual soil activities of 15.2 to 11.5 pCi/g (Table 9). An additional extraction did not mobilize any incremental amounts of  $^{137}\text{Cs}$  activity. These data suggested that the limits of  $^{137}\text{Cs}$  removal in Batch II soil material ranged from about 43 – 57%

**Table 7.** Selective Extraction of  $^{137}\text{Cs}$  from JN Site and Hanford Soils

Forms of $^{137}\text{Cs}$ associated with soil fractions	JN Site Soils <sup>a</sup>		Hanford Soils <sup>b</sup>		
	Batch I (%)	Batch II (%)	116-C-1 (%)	116-D-1B (%)	116-F-4 (%)
Water soluble	0	--	--	--	--
Mg-chloride extractable	<0.2 <sup>c</sup>	<6 <sup>c</sup>	0.5	2.0	0.9
Acidic Na-Ac Soluble	<0.3 <sup>c</sup>	<5 <sup>c</sup>	0.8	2.4	0.9
Oxidizing acid soluble	0.3	<7 <sup>c</sup>	11.3	21.1	8.4
Reducible acid soluble	0.1	<6 <sup>c</sup>	9.7	15.6	3.1
Unextractable <sup>d</sup> (%)	>99.1	>76	77.7	58.9	86.7

<sup>a</sup>JN Site soils from Ohio are derived from glacial till and fine textured (45 – 70% silt and Clay).

<sup>b</sup>Hanford Site soils from Washington are derived from riverine and flood deposits and are relatively very coarse textured (1 – 6% silt and clay). Source: Mattigod et al. (1994 a, b).

<sup>c</sup> $^{137}\text{Cs}$  in extracts was below minimum detectable activity (MDA).

<sup>d</sup>Recalcitrant fraction.

**Table 8.** Lixiviant Extractable  $^{137}\text{Cs}$  in Batch I Soil from JN Site

Extraction Stage <sup>a</sup>	Activity in solution (pCi/g)	Activity removed (pCi)	% of Initial Activity removed	Cum % Init Activity removed	Residual Activity in soil (pCi/g)	% residual Activity removed
0	--	--	--	--	609.20 <sup>b</sup>	--
1	29.12	5824	22.3	22.3	473.16	22.3
2	27.96	5592	21.4	43.7	342.54	27.6
3	20.04	4008	15.4	59.1	248.91	27.3
DI water rinse	3.23	1657	6.4	65.5	210.20	15.6

<sup>a</sup>Two hundred grams of lixiviant was used during each step to extract 42.81 grams of soil, and after the third extraction, 513 grams of water was used to rinse the soil free of spent lixiviant.

<sup>b</sup>Activity of sample composited from Bags 1- 3.

**Table 9.** Lixiviant Extractable  $^{137}\text{Cs}$  in Batch II Soil from JN Site

Extraction Step	Soil (g)	Lixiviant I Step (g)	Lixiviant II Step (g)	Total Mass Lixiviant (g)	Residual Activity in soil (pCi/g)	Activity removed (%)
0	--	--	--	--	26.49	--
1	40.84	200	--	200	11.45	56.8
1 (Dup)	40.84	200	--	200	15.20	42.6
2	40.84	200	200	400	12.80	51.7

### Optimization of Lixiviant Composition

The data showed that with increasing concentration of HH lixiviant component from 0.1 to 0.25 M resulted in increasing percentage of  $^{137}\text{Cs}$  removal (~12 to ~38%) from Batch I soil (Table 10, Figure 8). Increasing HH concentration beyond 0.25 M did not result in any significant increases in  $^{137}\text{Cs}$  mobilization. These tests showed that the maximal  $^{137}\text{Cs}$  removal for Batch I soil did not exceed on average ~40% of the initial activity

The results of the CA component optimization tests showed that with no CA added, only ~17% of  $^{137}\text{Cs}$  present in the Batch I soil could be released into the solution phase (Table 10, Figure 9). However, adding CA component in increasing concentrations resulted in concomitant increases in  $^{137}\text{Cs}$  mobilization until a maximal removal of ~40% was achieved at CA concentrations  $\geq 1.0$  M.

These tests indicated that a single extraction with the optimized PNNL lixiviant can remove more than a third of the  $^{137}\text{Cs}$  activity originally present in the sections of the JN site soil (such

as Batch I) that contained the highest activity. The results also indicated (Table 10, 3 successive extraction tests with 0.1M HH) can cumulatively remove more  $^{137}\text{Cs}$  activity from the soil.

Finally, these data suggested that the optimally performing PNNL lixiviant can be formulated to achieve maximum extraction (~40%) of  $^{137}\text{Cs}$  from Batch I soil with minimal concentration of components (~0.25M HH, ~1M CA, and 0.3M of NC), when the extractions are conducted at 90 °C with a reaction time (contact or residence time) of 3 hours.

**Table 10.** Lixiviant Optimization Test Results

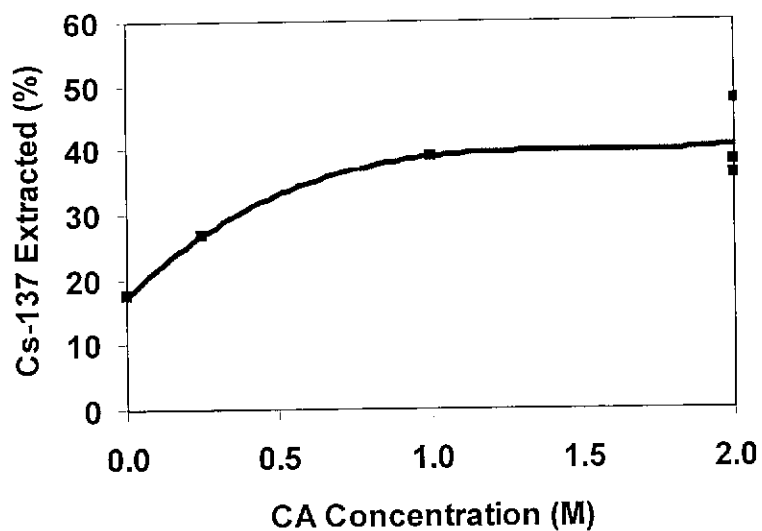
Lixiviant Component Concentration (M)			Wt of Soil (g) dry basis	Initial Activity (pCi/g)	Total Initial Activity (pCi)	Final Act (pCi/g)	Total Residual Activity (pCi)	$^{137}\text{Cs}$ Act. Removed (%)
HH	CA	NC						
0.10	2.00	0.30	100	682.0	68200	--	--	10.1 <sup>a</sup>
0.10	2.00	0.30	100	682.0	68200	--	--	27.2 <sup>b</sup>
0.10	2.00	0.30	100	682.0	68200	--	--	38.3 <sup>c</sup>
0.10	2.00	0.30	100	682.0	68200	589.0	58900	13.6
0.25	2.00	0.30	100	682.0	68200	436.8	43680	36.0
0.25	2.00	0.30	100	682.0	68200	423.4	42340	37.9
0.25	2.00	0.30	100	682.0	68200	358.0	35800	47.5
0.50	2.00	0.30	100	682.0	68200	421.2	42120	38.2
0.50	2.00	0.30	100	682.0	68200	401.0	40100	41.2
0.75	2.00	0.30	100	682.0	68200	417.0	41700	38.9
0.25	0.00	0.30	100	682.0	68200	564.0	56400	17.3
0.25	0.25	0.30	100	682.0	68200	500.0	50000	26.7
0.25	1.00	0.30	100	682.0	68200	417.0	41700	38.9

All were single extractions except as noted.

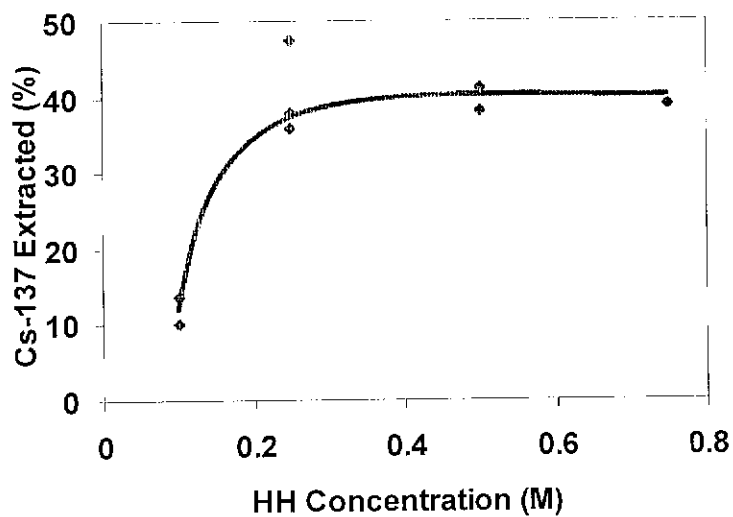
<sup>a</sup>Calculated from counting spent lixiviant after 1 extraction

<sup>b</sup>Cumulative  $^{137}\text{Cs}$  removal calculated from counting spent lixiviant after 2 successive extractions.

<sup>c</sup>Cumulative  $^{137}\text{Cs}$  removal calculated from counting spent lixiviant after 3 successive extractions



**Figure 8.** Extraction of  $^{137}\text{Cs}$  from Batch I Soil as a Function of HH Concentration in Lixiviant



**Figure 9.** Extraction of  $^{137}\text{Cs}$  from Batch I Soil as Function of CA Concentration in Lixiviant.

**Table 11.** Optimized Lixiviant Flow-through Test Data for Batch I Soil Sample

Lix Vol (ml)	No. bed vol	No. pore vol	Soil wt oven dry basis (g)	Init. <sup>137</sup> Cs Act. <sup>a</sup> (pCi/g)	Ini. Total Act (pCi)	<sup>137</sup> Cs Act in Spent Lixiviant (pCi/ml)	Total <sup>137</sup> Cs removed (pCi)	% Act removed
82	4.5	10	26.18	559	14635	22.7	1861	12.7
164	9.0	20	26.18	559	14635	9.9	1630	11.1
246	13.5	30	26.18	559	14635	11.1	2731	18.7
410	22.5	50	26.18	559	14635	9.9	4043	27.6

Soil Column contained 28.9 g of moist soil (~10.4 % moisture content) packed to a depth of 2 cm.

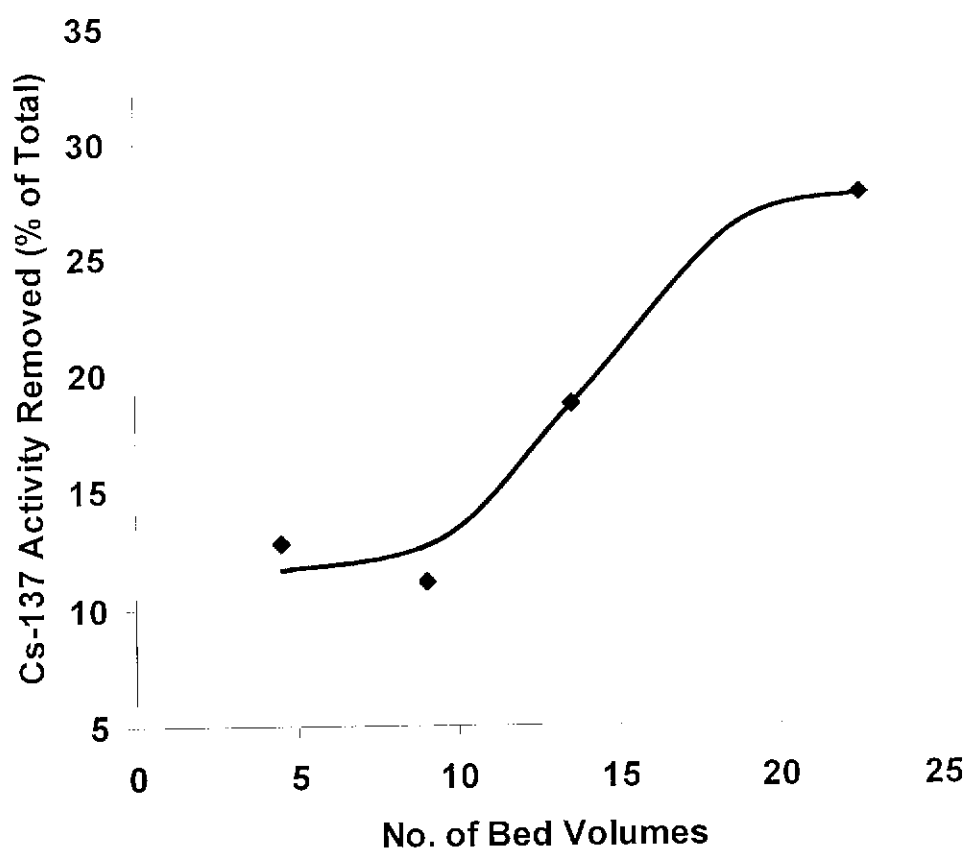
<sup>a</sup>Batch I soil sampled from Bag 3.

### Lixiviant Flow-Through Tests

The results of the column tests (Table 11, Figure 10) indicated that increasing bed volumes of lixiviant passing through the column mobilized increasing fractions of (~11 to ~28 %) of <sup>137</sup>Cs from the Batch I soil. The data also showed that there was no significant difference in fraction of <sup>137</sup>Cs extracted at bed volumes  $\leq 9$ . Typically, in flow-through systems, the measured extraction efficiencies are less than what was observed in well-mixed batch extraction systems. Such lower extraction efficiencies in advective flow-through systems can be ascribed to; 1) lower soil particle surface area accessible to extraction, and 2) activity trapped in dead-end pores which would be inaccessible to lixiviant.

The maximum fraction of <sup>137</sup>Cs extractable from Batch I soil under flow-through conditions was ~28%. These data indicated that to achieve maximal <sup>137</sup>Cs mobilization (~28%) from a soil column consisting of Batch I type of soil, it would be necessary to advectively-flow at least ~20 bed volumes of optimized lixiviant.





**Figure 10.** Extraction of  $^{137}\text{Cs}$  from Batch I Soil as function of Bed Volume of Lixiviant passed through the Soil Column

## CONCLUSIONS

Physical, chemical, mineralogical and radiochemical characterization and  $^{137}\text{Cs}$  extractability tests were conducted on soil samples from the JN site in West Jefferson Ohio. The results indicated that,

- The Batch I soil material was well-graded with silt and clay content of 45% whereas, Batch II and Batch III soils were finer textured with silt and clay content of ~67 - 70%.
- Organic carbon content of all three (Batch I, II, and III) soil samples were similar (~1 - 2%), except that Batch I soil contained 3 – 5 times more inorganic carbon than Batch II soil.
- The dominant minerals in these soils were quartz and dolomite, calcite, and hornblende with minor quantities of feldspar, mica, chlorite and smectite. Batch I material contained more dolomite and calcite, whereas, the Batch II soil contained relatively higher proportions of mica and hornblende than the Batch I soil.
- A major fraction of  $^{137}\text{Cs}$  activities (~86% of the total activity) in Batch II and III soils were present in silt and clay fractions (~68% of mass). The sand and gravel fraction which constituted ~30 -33% of Batch II and III soil mass contained only ~14% of the total  $^{137}\text{Cs}$  activities in these soils.
- Selective extractions with conventional electrolytes were relatively ineffective in mobilizing  $^{137}\text{Cs}$  indicating that almost all of this contaminant in these soils is in recalcitrant (immobilized) forms such as in interlayer edge and structural sites of micas.
- Three successive extractions using the PNNL lixiviant removed a total of ~66% of initial activity from Batch I soil resulting in a residual  $^{137}\text{Cs}$  activity of about 210 pCi/g. in soil. The PNNL lixiviant was effective in mobilizing and removing significant fractions of relatively recalcitrant forms of  $^{137}\text{Cs}$  in this soil.
- A single extraction using an enhanced PNNL lixiviant removed about 43 – 57% of the  $^{137}\text{Cs}$  activity from Batch II soil with resulting residual soil activities of 11.5 - 15.2 pCi/g.
- Lixiviant optimization batch experiments conducted using Batch I soil (containing the highest  $^{137}\text{Cs}$  activity at the JN site) indicated that a maximum fraction (~40%) of  $^{137}\text{Cs}$  can be mobilized with the minimum concentrations of lixiviant components consisting of ~0.25M HH, ~1M CA, and 0.3M of NC respectively
- Dynamic flow tests conducted using the optimized PNNL lixiviant indicated that the maximum fraction of  $^{137}\text{Cs}$  extractable from Batch I soil under flow-through conditions was ~28% as compared to a maximum of ~40% extraction achieved in optimized batch experiments. These data indicated that to achieve maximum  $^{137}\text{Cs}$  mobilization from Batch I type soil containing high  $^{137}\text{Cs}$  activity (~559 pCi/g), it would be necessary to advectively-flow at least ~20 bed volumes of optimized lixiviant through the soil column.

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